The impact of molecular chemistry on understanding the new physics found in magnetic materials based on organic molecules is starting to be appreciated.

Organic Ferromagnets

Dante Gatteschi

Department of Chemistry
University of Florence, Italy

The magnetic materials which are currently used in our everyday life are usually inorganic and based on metallic or ionic lattices. Iron, SmCo$_5$ and Nd$_2$Fe14$_B$ are typical examples of metallic (intermetallic) materials, while magnetite, γ-Fe$_2$O$_3$ and CrO$_2$ represent ionic materials. They each have the properties of inorganic materials, being heavy, opaque and hardly soluble in water and even less so in organic solvents.

In the last few years, chemists have started an ambitious programme of designing and synthesizing new classes of magnetic materials using the techniques of molecular organic chemistry. For sure, a strong stimulus for taking up the challenge came from the synthesis of polymeric and charge-transfer organic compounds which behave as conductors and superconductors. For if organic molecules can have some properties which are usually associated with inorganic materials, why should they not be magnetic? Moreover, these new materials could in principle give rise to novel properties. An organic magnet may be soluble in organic solvents, easily processed, biocompatible, transparent, and its magnetic properties could conceivably be fine-tuned using organic chemistry.

This overview of aims to show the extent to which new physics is encountered in this family of novel compounds since the concerted efforts of chemists and physicists will be needed to fully appreciate the enormous potential arising from the impact of molecular chemistry on organic ferromagnetism.

3-d Spin Structure Preferred

The most common procedure among the several available for obtaining a molecular organic ferromagnet (ferrimagnet) involves assembling molecular building blocks, in principle as in a LEGO toy (a schematic representation is shown in Fig. 1). The building blocks must have individual spins (either metal ions or organic radicals) and they must be assembled in a proper three-dimensional arrangement in such a way that the preferred spin orientation, determined by intermolecular exchange interactions, gives rise to a non-zero magnetic component. In fact, bulk magnetic properties such as ferromagnetism and ferrimagnetism are determined by three-dimensional interactions, and can be only observed when these are present.

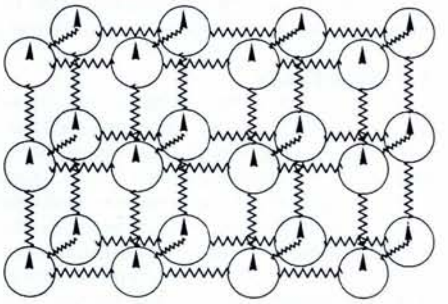

Fig. 1 — A schematic representation of what is needed to assemble a molecular organic ferromagnet: the appropriate blocks must be assembled in a three-dimensional arrangement to have their spins parallel to each other (or antiparallel to each other if the individual spins are different).

In Fig. 1, the springs represent the appropriate interaction connecting the building blocks. As we shall see, it has proved very difficult up to now to create a three-dimensional network of spins in molecular systems; low-dimensional magnetic materials have usually been produced. While this limitation may have depressed the observed critical temperatures T_c below which they become magnetic, several interesting new classes of materials have been obtained nevertheless. Secondly, apart from one notable exception, the systems investigated so far are insulators, where the magnetic interactions between the building blocks are essentially of the exchange type with all its the possible variants including direct exchange, super-exchange and spin polarization. In insulators, the unpaired electrons are usually localized on individual atoms and/or on individual molecular orbitals (magnetic orbitals): the magnetic interactions essentially depend on the relative orientations of the magnetic orbitals. As a simple rule, we can say that if the unpaired electrons are in orthogonal magnetic orbitals they keep their spins parallel to each other (they are coupled *ferromagnetically*). On the other hand, if the magnetic orbitals have a non-zero overlap, a weak covalent bond is formed and the spins are antiparallel to each other (they are coupled *antiferromagnetically*).

A third feature is that organic radicals tend to be unstable molecules, because they usually interact in pairs forming covalent bonds which pair the spins of the two electrons. It is therefore necessary to force the radicals to interact while keeping their spins parallel to each other. We shall see that this is invariably not an easy task, although some important success has already been achieved.

Two Limiting Approaches for Synthesis

The procedure for synthesizing organic ferromagnets involves reacting either individual building blocks, which have an independent existence, or simple moieties that can be indicated on paper, but which do not survive independently. From a structural point of view, the materials can be described as ranging from molecular (the lattice is composed of weakly interacting molecules) to covalent (the structural patterns present in the lattice are connected by strong covalent bonds). In either case the organic part represents a fundamental element of the whole architecture.

Two, different, limiting approaches have been adopted for syntheses; they can be distinguished by the centres containing the unpaired electrons. In the first, these centres are metal ions, and the organic molecules are formally diamagnetic and act as bridges between them. Thus in the scheme of Fig. 1,

Glossary

Hund's rule	Electrons in orthogonal orbitals keep their spins parallel to each other.
Ferromagnetism	Ordered state in which all the spins in a lattice are parallel to each other. It is characterized by spontaneous magnetization.
Ferrimagnetism	Ordered state in which at least two sublattices, comprising different individual spins are present. The spins within a sublattice are parallel to each other, but antiparallel to those of the other sublattice. It is characterized by spontaneous magnetization.
Antiferromagnetism	Ordered state in which at least two sublattices, comprising identical individual spins, are present. The spins within a sublattice are parallel to each other, but antiparallel to those of the other sublattice.
Heisenberg exchange	Isotropic magnetic interaction between two spins. It can be represented by the Hamiltonian $H = J\,\boldsymbol{S}_1.\boldsymbol{S}_2$. where J is the isotropic coupling constant.
Super-exchange	Magnetic interaction transmitted by formally diamagnetic atoms or groups of atoms.

Dante Gatteschi has been a Professor of Chemistry in the Chemistry Department, University of Florence, Via Maragliano, 75/77, I-50144 Florence, since 1980. He was educated at the university and joined the department as an Assistant in 1969, becoming a Lecturer in 1976. He has co-edited two books on magnetic properties and co-authored (with A. Bencini) *EPR of Exchange Coupled Systems* (1990). Professor Gatteschi serves on the editorial boards of the *New J. of Chem.*, *J. Mater. Chem.*, and *Adv. Mater.*

the organic molecules are the springs connecting the metal ions which act as the building blocks. In the second approach, the magnetic centres are organic radicals so it can be called organic ferromagnetism (the first is more correctly termed molecular ferromagnetism). Between these two limits there lies a wide variety of other approaches using both organic radicals and metal ions. The material with the highest critical temperature reported so far was produced using one such hybrid approach.

In the first approach, the organic molecules bridge metal ions so they take the place of the oxide ions in the classical inorganic magnets; they transmit the magnetic interactions through super-exchange mechanisms. There is nothing really new in these materials from a conceptual point of view except that some organic molecules can transmit magnetic interactions over very long distances. For instance, oxalate bridges as shown below can transmit antiferromagnetic exchange interactions between two copper ions corresponding to an energy of interaction of 500 K, and between a copper ion and a manganese ion corresponding to 250 K even if the metal-metal distance is longer than 5 Å (the energy of interaction in degrees Kelvin can be transformed into other energy units using 1 K ~ 0.69 cm^{-1} ~ 20.8 GHz ~ 1.38 x 10^{-21} J). Oxalate bridges can also transmit ferromagnetic coupling between metal ions. This occurs, for instance, between Cr (III) and Ni(II). The former has a d^3 configuration with three unpaired electrons in xy, xz, and yz orbitals, while the latter has a d^8 configuration with two unpaired electrons in x^2-y^2 and z^2 orbitals. Since the two sets of orbitals are orthogonal their spins prefer to stay parallel to each other according to Hund's rule. The energy of the ferromagnetic interaction is approximately 10 K.

Several Families of Materials

Oxalates

In Fig. 2, the molecules ***1***, ***2***, and ***3*** depict some of the oxalate building blocks which have been used to obtain bulk ferro- or ferrimagnets. In ***1*** it is the oxalate itself which is used, while in ***2*** and ***3*** the organic molecules are derivatives of oxalates. This shows the versatility of organic chemistry in giving different structures with minor changes to the building blocks. The importance of these building blocks is that they can bind to other metal ions forming extended structures using outer oxygen atoms. Molecule ***1*** is structurally different from ***2*** and ***3*** because it easily forms three-dimensional structures (the additional bonds arise in three different directions in space) while the latter can only readily form chain structures.

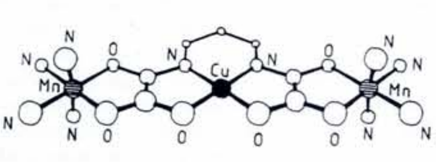

Fig. 3 — A segment of a ferrimagnetic chain formed by alternating Cu(II) and Mn(II) ions. The metal ions are antiferromagnetically coupled but the individual moments are different and are therefore uncompensated.

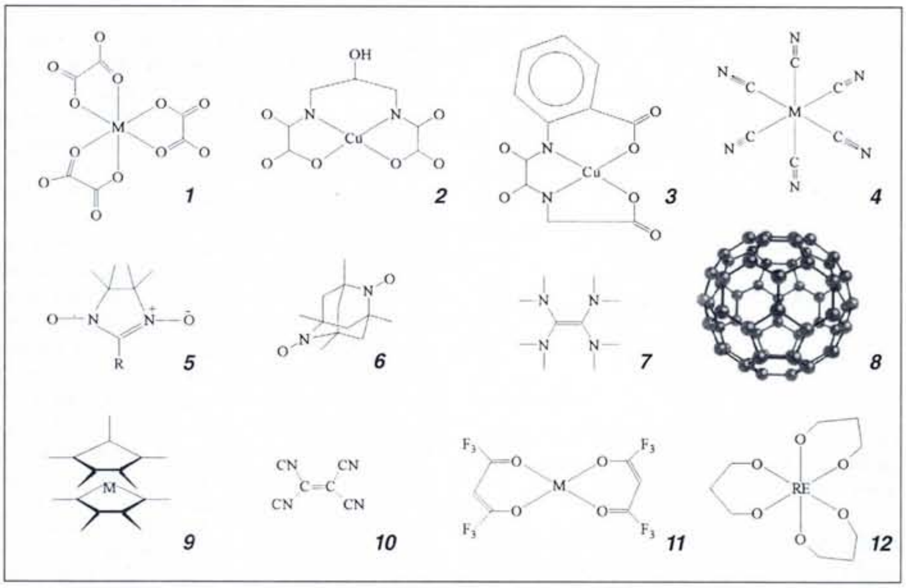

Fig. 2 — Some of the building blocks used so far for molecular ferromagnets.

Particularly spectacular results have been obtained with the building blocks ***2*** and ***3*** added to manganese ions to give chains of alternating copper and manganese ions, as shown in Fig. 3. Since Cu(II) with a ground-state spin S = 1/2 and Mn(II) with S = 5/2, are antiferromagnetically coupled the ground state for the chain corresponds to having all the manganese spins up and all the copper spins down, yielding a one-dimensional ferrimagnet. Indeed, a similar chain was the first reported example of a one-dimensional ferrimagnet. Weak interchain interactions allow the system to order as a bulk ferromagnet at temperatures as high as 4.6 K. However, the principal breakthrough in this approach involves the use of asymmetric organic molecules having one end which can selectively bind to a particular metal ion while the other end binds to a different metal ion. A new material ordering at 30 K was obtained on dehydrating the solid. It can be assumed that dehydration leads to shorter inter-chain distances so the increase in the critical temperature is a result of stronger inter-chain interactions. Very recently, two-dimensional structures were achieved by employing modified ligands [1].

Prussian Blue analogues

Building block ***4*** has also been used. The structural motif, a hexacyanide, is found in well-known compounds such as Prussian Blue. The nitrogen atoms of the cyanides can bind to other metal ions, and cubic compounds of formula MM'(CN)$_x$ can be obtained. According to the nature of M and M', ferro-, ferri- and antiferro-magnets can be obtained. The highest critical temperatures reported so far [2], 240 K for the ferrimagnet [Cr$_5$(CN)$_{12}$]10H$_2$0, are already close to room temperature, but in this case the role of organic chemistry is rather meager (is a cyanide organic or inorganic?).

Nitroxides

On the purely organic side the first example of a bulk ferromagnet [3] is provided by a variant of building block ***5***, namely p-nitrophenyl nitronyl nitroxide, which in the β-phase orders at 1 K. Understanding why these organic molecules order ferromagnetically, while generally preferring to couple their spins in a covalent bond, has been rather intriguing and shows how ingenuity (serendipity) can give rise to counter-intuitive behaviour. The unpaired electron in a molecule such as ***1*** spends essentially all its time on the two NO groups, but some unpaired spin density is delocalized on the rest of the molecule. Now, in the structure of the compound which orders ferromagnetically, the distance between the NO group of one molecule and the phenyl group of another molecule is relatively short so regions of opposite spin density come close to each other, thus determining an overall parallel alignment of the spins present on the two NO groups, as shown in Fig. 4. While the interactions between the molecules are weak because the intermolecular distances are relatively long, it is certainly surprising that organic molecules, which usually do not have unpaired electrons, can be assembled in a way that keeps all their unpaired spins parallel to each other.

It should be noted in passing that the radical molecules in the γ-phase are arranged

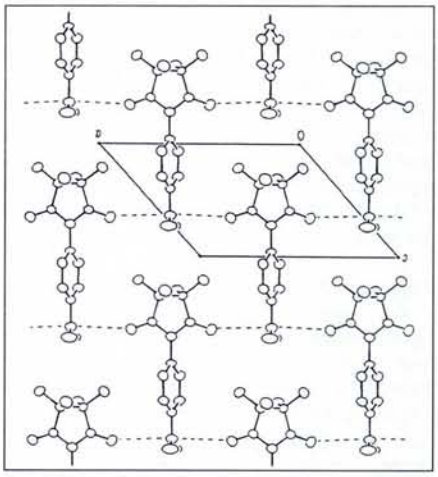

Fig. 4 — A sketch of the β-phase of p-nitrophenyl nitronyl nitroxide.

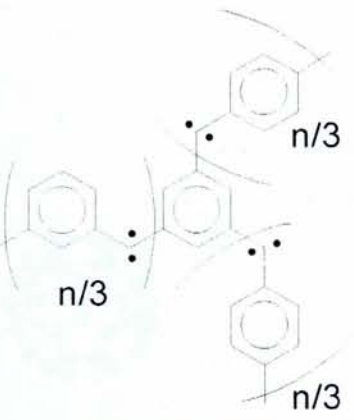

Fig. 5 — A sketch of the structure of a polycarbene containing eighteen unpaired electrons with a $S = 9$ ground state.

in chains and that at relatively high temperatures they behave as one-dimensional Heisenberg ferromagnets, indeed perhaps the best available. Slightly higher critical temperatures were reported recently [4] for molecule **6**.

Polycarbenes

The ingenuity of organic chemists has shown that it is possible to do better, in terms of interactions between individual magnetic centres, by synthesizing [5] the molecule depicted in Fig. 5. With twelve unpaired electrons which are strongly coupled to give a ground $S = 9$ state with no evidence of any thermally populated state, this is the highest member of the series available at the moment. In this case, the building blocks are carbenes (molecules which contain one carbon atom with *two* unpaired electrons in two orthogonal orbitals) arranged in such a way that the ground state is a triplet. If these building blocks are assembled so that the magnetic orbitals remain orthogonal to each other, the ground state must according to Hund's rule be that of the highest multiplicity; a high-T_c organic ferromagnet would result if the building blocks could be assembled in three dimensions. The concept is simple on paper, but unfortunately chemistry is significantly more complicated.

Fullerene

Recently the fullerene revolution touched also molecular magnetism, and intercalation of TDAE in the fullerene C_{60} (**7** and **8**) was found to allow ferromagnetic ordering at about 19 K [6]. This case however is different from all the previous ones, because instead of being an insulator TDAE C_{60} is a conductor so that the interaction responsible of the parallel alignment of the spins should be itinerant magnetism.

Organometallics

An organometallic approach was taken up for building blocks **9** and **10**, *i.e.*, the bulk ferromagnets were made by assembling in a regular way building blocks with unpaired electrons on both the metal ions and the organic molecules. The first reported molecular ferromagnet [7] was $[Fe(Me_5Cp)]^+(TCNE)^-$ where Me_5Cp is pentamethyl-cyclopentadienide, see Fig. 6, and $(TCNE)^-$ is is an abbreviation for molecule **10**. As shown Fig. 6, this material has a column structure in which the building blocks **9** and **10** alternate regularly. The nature of the interaction responsible of the ferromagnetic coupling has been a source of some controversy, but it now seems to be accepted that the unpaired spin density on the metal ion polarizes the five-membered carbon rings of Me_5Cp in such a way that some negative spin density is present on the carbon atoms. This negative spin density interacts with the positive spin density on **10** in such a way that the spin of each succeeding metal ion in the rows of molecules is parallel to that of its predecessor.

In an attempt to use a variant of building block **9**, Miller *et al.* [8] from Dupont used $V(C_6H_6)_2$ where the five-membered rings are substituted by benzene rings. However, a different compound was obtained, with a formula $V(TCNE)_2$. This compound orders ferrimagnetically at a surprisingly high temperature (above 400 K!). It is not a crystalline material, so it behaves as a disordered ferrimagnet. The vanadium ion seems to have a +2 oxidation state and to be bound to TCNE through the nitrogen atoms with weak covalent bonding. It is also interesting to note that all the derivatives which have been obtained subsequently by changing the organic molecule inevitably order at lower temperatures.

Nitronyl nitroxides and transition metal ions

Finally, there is the family of molecular ferrimagnets which are assembled using building blocks **5** (called NITR for short, where NIT indicates 4,4,5,5-tetramethyl-imadazoline-1-oxyl-3-oxide, and R the subsequent group in position 2), with either **11**, $M(hfac)_2$, or **12**, $RE(hfac)_3$, where M is a transition-metal ion, RE a rare-earth ion, and hfac denotes hexafluoroacetylacetonate. Molecule **5** can bind to two different metal ions, using its two oxygen atoms, yielding columns in which the electron spins of the organic component alternate regularly in space with the those of the metal ions (a typical structure is shown in Fig 7). When M = Zn or Y, $S = 0$ and the compounds behave as an almost ideal one-dimensional Heisenberg antiferromagnet due to the coupling between the radicals mediated by the intervening diamagnetic metal ions. The interaction energy is approximately 15 K even if the distance of the shortest approach between the radicals is larger than 4 Å. When M = Cu(II), $S = 1/2$ and the chains behave as one-dimensional ferromagnets due to the interactions between Cu(II) and radicals which typically correspond to an energy of 20-70 K. It may seem surprising at first sight that the coupling between the radical and the metal ion to which it is directly bound is ferromagnetic. The reason is that the unpaired electron on the radical is in a π^* molecular orbital orthogonal to the x^2-y^2 orbital of Cu(II) so according to Hund's rule, the two spins are parallel to each other. The materials do not order magnetically above 1.2 K because only weak interactions are operative between chains. In fact, the hfac groups are bulky and the CF_3 groups are hardly available for transmitting exchange interactions.

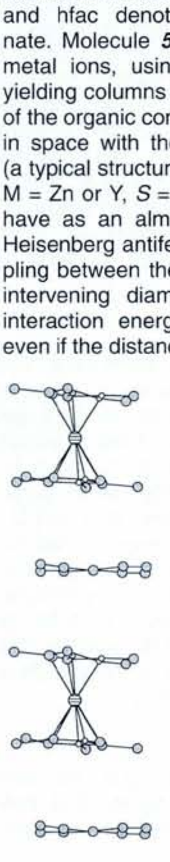

Fig. 6 — A sketch of the structure of $[Fe(Me_5Cp)]^+(TCNE)^-$. The cations and anions regularly alternate along a chain and they are ferromagnetically coupled. Weak contacts between chains determine the cross-over to bulk ferromagnetism.

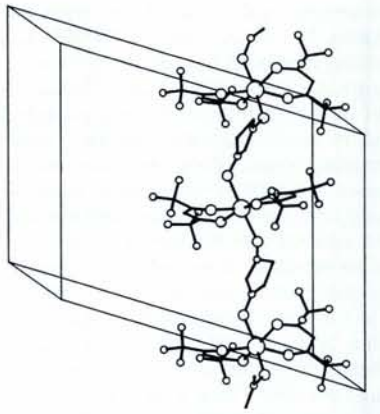

Fig. 7 — A sketch of a typical structure in which $M(hfac)_2$ moieties alternate regularly in a chain. The chains are kept well separated from each other by the bulky CF_3 groups of the hfac molecules.

When M = Ni(II) or Mn(II) we have $S = 1$ or 5/2, respectively, and the compounds behave as one-dimensional ferrimagnets (because the metal-radical interaction is antiferromagnetic) with energies of 300 K for Ni and 600-700 K for Mn. There is at least one magnetic orbital with a finite overlap with the radical's magnetic orbital, thus ensuring an antiferromagnetic coupling.

The $[Mn(hfac)_2(NITR)]$ derivatives have been thoroughly investigated. $[Mn(hfac)_2$-$(NITiPr)]$, where iPr is an iso-propyl group, has a straight-chain structure and behaves as an ideal one-dimensional Heisenberg ferrimagnet as evidenced by electron paramagnetic resonance (EPR) and NMR spectra showing that the spin dynamics at high temperatures are dominated by diffusive effects. These two spectroscopies monitor the correlation between the spins in magnetic materials. If a given spin is perturbed from its equilibrium position in a ideal one-dimensional material, the magnetization will return to equilibrium through a concerted movement of all the spins in the chain analogous to that of diffusion in liquids, giving rise to a particular lineshape and relaxation in magnetic resonance. The behaviour shows that the ratio between the intra- and inter-chain coupling constants is larger than 10^6. It is therefore only the weak dipolar interactions between the chains which determine the cross-over from one-dimensional behaviour to three-dimensional order. In fact, at the critical temperature (7.6 K) for bulk ferrimagnetic order, the spin-correlation length extends to about 200 Mn-radical pairs. The short-range order effects observed in these materials are unique.

[Mn(hfac)$_2$(NITEt)], where the radical Et is an ethyl group, has a zig-zag chain structure and as a consequence a less ideal one-dimensional behaviour, as again evidenced by EPR and NMR spectra. [Mn(hfac)$_2$-(NITPhOMe)], where PhOMe denotes a para-methoxy-phenyl group, has an interesting helical structure: it crystallizes in the P3$_1$ space group which means that a centre of symmetry is lacking. As such it can be expected to give rise to non-linear optical properties. There is in fact a sizeable second harmonic generation coefficient. This property is associated with the organic moiety, the metal ions being there to ensure asymmetric ordering of the radicals in the crystals. Another interesting property of [Mn(hfac)$_2$(NITPhOMe)] is optical activity in the paramagnetic phase. Since there must be Faraday rotation in the ordered phase it would be interesting to investigate the interplay of the two properties, which are present together in the same compound for the first time. This is a clear example of the coexistence of different properties in molecular organic magnets which is not found in the classic inorganic magnets.

The three [Mn(hfac)$_2$(NITR)] compounds order magnetically at 7.6 K (R = iPr), 8.4 K (R = Et), and 4.8 K (R = PhOMe). The variation in the critical temperature is associated with the structural variation, which affects the magneto-crystalline anisotropy. As the variation is brought about by changing the peripheral R group, this suggests that it may be possible to fine-tune the magnetic properties of organic magnets by controlling the chemistry [9].

Nitronyl nitroxides and rare-earth ions

Several surprises are encountered with building block ***12***. From the structural point of view its derivatives form columnar compounds similar to those of the transition-metal ions, with the rare-earth ions and the organic radicals alternating in a regular way in space. The first surprise was found with [Gd(hfac)$_3$(NITEt)]. Assuming nearest-neighbour interactions along the chains, the compound might behave either as an one-dimensional ferromagnet (for parallel alignment of the spins) or as a ferrimagnet (for antiparallel alignment of the spins) since the individual magnetic moments are compensated. However, experiments have shown that the compound behaves as an *antiferromagnet*. This can be rationalized by introducing antiferromagnetic next nearest-neighbour interactions between both pairs of radicals and pairs of rare-earth ions. In this way, a given spin is under the conflicting influence of opposing interactions, and is strongly frustrated. This situation has long been theoretically predicted, but very few compounds exhibiting frustration have been identified. Since Gd(III) is an isotropic ion with $S = 7/2$, [Gd(hfac)$_3$(NITEt)] is an excellent example of a one-dimensional Heisenberg magnet with conflicting interactions. For the moment only the simplified Ising model has been worked out for the case of different spins interacting also with next nearest-neighbour ones. It has been found that the ground state can be described by a configuration with two neighbouring spins in the up direction, and the two following spins in the down direction. It is also likely that for the Heisenberg case, a helical configuration will have the lowest energy.

The energy of the metal-radical interaction is ferromagnetic, with an energy of about 5 K, while the radical-radical and the metal-metal interactions are antiferromagnetic. The energy of the first is approximately 15 K while the metal-metal exchange interaction mediated by the radical is of the order of 10 K, a value which is surprisingly high for rare-earth ions where the inner 4f magnetic orbitals are well shielded from the interactions with the ligands.

The materials obtained by substituting the isotropic Gd(III) ions with, for instance, anisotropic rare-earth ions such as Dy(III) also behave as antiferromagnets. Perhaps more surprising than the observation of confusion is that [Dy(hfac)$_3$(NITEt)] orders as a weak ferromagnet at 4.2 K. Compare this with the behaviour of simple dysprosium salts such as Dy(OH)$_3$ which order due to dipolar interactions as ferro- or antiferromagnets at temperatures which do not exceed 5.2 K. The Dy-Dy distances in these hydroxides are fairly small (in the range of 3 Å) while in [Dy(hfac)$_3$(NITEt)] the shortest intra-chain Dy-Dy distances are much larger (8.74 Å) and the inter-chain ones are 10.76 Å. It seems that the weak dipolar interactions in [Dy(hfac)$_3$(NITEt)] are enhanced by the strong magneto-crystalline anisotropy but also by correlation between the spins of the metal ions within the chains [10].

The investigation of organic ferromagnets is just beginning and the concerted efforts of chemists and physicists are needed to fully appreciate the enormous potential arising from the impact of molecular chemistry on the solid-state physics of these novel materials. We expect that the principal lines of research in the next few years will involve attempts to increase the critical temperatures below which they become magnetic (by making more efficient three-dimensional structures) as well as more accurate investigations of material properties. It is especially in the field of the optical properties that major breakthroughs are expected.

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LHC Endorsement Provides Backing

Eighteen of CERN's nineteen Member States meeting in an extraordinary Council on 15 April endorsed a resolution envisaging participation by non-member states and the creation of a special statute that gives them voting rights. Also endorsed were financing options proposed by C. Llewellyn Smith, CERN's Director-General. If non-member state participation materialises, CERN's next large accelerator — the LHC — could begin operating in 2002. The safety net is financing from CERN's ordinary budget with operation starting two years later (the four-year shutdown of LEP is the price one pays for LHC). A decision on financing can wait until 1997 when major investments begin.

The Member States clearly appreciated that there needed to be a firm statement of support for the LHC to back up the Director-General otherwise he would have a difficult time in negotiations with Japan and the USA. It is anticipated that formal voting on the LHC proposal will start at the next Council in June, shortly before proposals on LHC collaboration go to the US Congress in July. A High-Energy Advisory Sub-panel on the Future Vision of the US Program in Particle Physics, which reports to the US Department of Energy's High-Energy and Particle Physics Advisory Panel, has already announced the preliminary conclusions of its report which will be released in May. Agreement has been reached on two points following discussions with the particle physics community:

- Collaboration in LHC "would provide important opportunities... valuable use of technical progress achieved by the Superconducting Super Collider ... and the basis for further international collaboration".
- US vitality in the field will be assured by adequate funding to support effective running of existing and upgraded facilities.

The ordering is important because the US particle physics budget has been stripped bare following wholehearted commitment to the SSC before the project's termination.

Conjecture that Germany would not support the LHC at this stage turned out not to be true, although it hopes to know fairly soon the extra contributions the host countries will make. Spain did not endorse the resolution as it owes CERN some 150 MSFR, equivalent to two annual contributions, having contested the industrial returns. Council offered a 20% reduction in its contributions over the next 5 years provided the arrears are settled by June and the savings spent on building up the country's high-energy physics community, which Spain says is too small in relation to the CERN contribution.